# U.S. Fish and Wildlife Service Region 3 Contaminants Program

Swan Lake National Wildlife Refuge Contaminants Survey Results

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#### Abstract

Bullheads (Ictalurus sp.), carp (Cyprinus carpio), a quillback (Carpiodes cyprinus), a bigmouth buffalo (Ictiobus cyprinellus), and a turtle were collected from Elk, Honeyhouse, Turkey, and Yellow Creeks located on or near the border of Swan Lake National Wildlife Refuge near Sumner, Chariton County, Missouri. Whole fish samples and turtle fat and liver were analyzed for various metal and organic contaminants to determine if concentrations were elevated in the biota located on the refuge. Results were compared to the literature and potential contaminant problems were recognized.

Concentrations of copper, chromium, manganese, zinc, chlordane, and dieldrin either exceeded or were the same as concentrations in the literature where adverse effects to biota were reported. However, limited number of samples were collected at Swan Lake National Wildlife Refuge and different types of tissues were analyzed which may demonstrate the reason for higher concentrations. If concern is shown for populations of fish and wildlife resources using Swan Lake National Wildlife Refuge because of decreasing numbers or health, further investigations into these compounds should begin.

# Introduction

The National Wildlife Refuge System was established to acquire, protect, restore, and manage a diversity of habitats across the United States for the enhancement of important trust fish and wildlife resources. Even though refuges are managed specifically for fish and wildlife resources, the waters and land may be affected by contamination from offsite point and non-point sources of pollution. There is no direct evidence that contaminants are present in most refuge environments, but adjacent land uses may lead to the suspicion of contamination.

In 1987, a biological sampling program was initiated in Missouri to provide baseline characterization of contaminants in biological media collected on the four National Wildlife Refuges - Squaw Creek, Swan Lake, Mingo, and Clarence Cannon - and the National Fish Hatchery at Neosho. This program was conducted to determine if contaminant concentrations were elevated in biota on U.S. Fish and Wildlife Service (Service) lands and to identify existing contaminant problems and potential sources.

# Study Area

Swan Lake National Wildlife Refuge (SLNWR) is located near Sumner, in Chariton County, north central Missouri. The refuge currently consists of 4,268 ha (10,670 a) characterized as follows: about 800 ha (2,000 a) planted in corn, sorghum, clover, and wheat; 1,400 ha (3,500 a) managed in moist soil units; and the remaining acreage covered by water, forest, permanent grass, or native prairie (Service n.d.). No inorganic fertilizers or pesticides are used on the refuge and all crops are left in the fields for wildlife.

The refuge was established in 1937 to preserve habitat for ducks and prairie chickens. In 1941, Canada geese began to use SLNWR as a rest area during

migration and the refuge now has one of the largest concentrations of Canada geese in North America. The refuge is not only a rest stop for the geese, but has become the primary wintering area for the Eastern Prairie Population.

Swan Lake National Wildlife Refuge also supports many other species of wildlife, including about 40 species of mammals, and more than 230 species of birds (Service n.d.).

The topography of SLNWR is relatively flat and is subject to flooding from the Grand River and Yellow Creek, bordering the refuge. Three reservoirs and several creeks are contained on the refuge (Fig. 1). The reservoirs, Swan Lake, Silver Lake, and South Lake, are managed primarily for waterfowl. Gates and levees control the water flow between the reservoirs.

Silver Lake is the largest reservoir and is fed by a watershed of 286 km² (110 m²), 182 km² (70 m²) from Turkey Creek, and 104 km² (40 m²) from Elk Creek (FWS 1988). Water from Silver Lake can be drained to South Lake, Swan Lake, or the moist soil units. South Lake also receives water from an additional 33.8 km² (13 m²) watershed and Swan Lake, a 13 km² (5 m²) watershed.

The majority of the watershed of the reservoirs is intensively farmed. Major crops in the area are corn, milo, soybeans, and wheat. Railroads run along the western and southern boundaries of SLNWR. There are no large industries or known hazardous waste sites near the refuge or within its watershed.

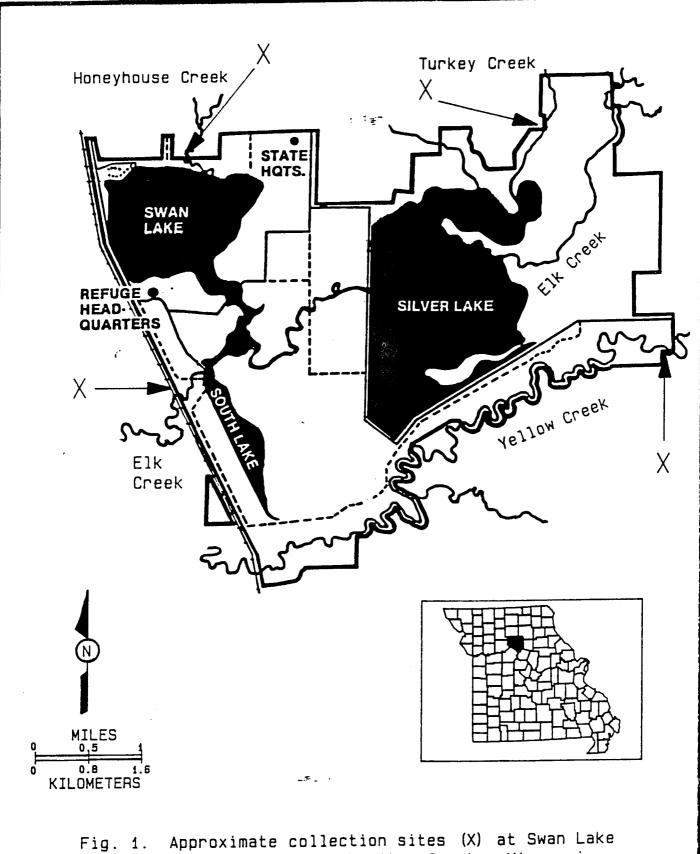
## Materials and Methods

Fish collections were conducted in June and July, 1987, at four sites along the SLNWR boundary (Fig. 1). Sites were chosen in waterways entering and exiting the refuge to determine if contaminants were entering and collecting in the refuge environment. Fish were seined and gill netted until adequate samples were obtained. Species containing high fat content were chosen to be analyzed.

Each fish was weighed to the nearest 0.1 g and measured (total length) to the nearest millimeter. The fish were then individually wrapped in aluminum foil, labeled, and stored on ice in a cooler while in the field. Upon returning to the office, the samples were frozen in a locked chest-style freezer unit. The samples were shipped on dry ice to the respective analytical laboratories with instructions on the type of analyses to be conducted and specific sample information.

A turtle was incidently caught in the nets while seining for fish. The turtle was transported on ice back to the office laboratory where the liver and fat were dissected from the carcass. The liver and fat were placed in individual chemically-cleaned glass jars, frozen with the fish, and shipped with the fish samples for analyses.

Sample analyses were completed by three different contract laboratories. The Service's Patuxent Analytical Control Facility (Patuxent) awards the contracts based on quality assurance and quality control (QA/QC) results from analytical



National Wildlife Refuge, Chariton County, Missouri.

procedures conducted. Patuxent monitors the performance of the laboratories during the analyses and has confidence in the accuracy of the data. Laboratory quality control reports document the laboratories' performance on spikes, blanks, and duplicates.

The Environmental Trace Substances Research Center, Columbia, Missouri conducted the analyses for metal residues in the samples. An atomic absorption spectrophotometer technique was conducted to measure levels of arsenic, mercury, and selenium residues. Levels of aluminum, beryllium, cadmium, chromium, copper, iron, lead, manganese, nickel, thallium, and zinc were scanned using an inductively coupled plasma atomic emission spectrophotometer. Detection limits are listed in Table 1. Results are reported in parts per million (ppm) dry weight unless otherwise stated.

Organochlorine and PCB residue analyses were conducted by Mississippi State Chemical Laboratory (MSCL), Mississippi State, Mississippi, and Weyerhaeuser Analytical and Testing Services (WATS), Takoma, Washington. Both laboratories conducted their analyses using methods prescribed in Patuxent protocols for organochlorine and PCB residue scans using a gas chromatograph. Organochlorine residues analyzed at MSCL included p,p' DDE, p,p' DDD, p,p'DDT, o,p' DDE, o,p' DDD, o,p' DDT, dieldrin, endrin, heptachlor epoxide, cischlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, toxaphene,  $\alpha$ -benzene hexachloride (BHC),  $\beta$ -BHC,  $\Delta$ -BHC,  $\gamma$ -BHC, hexachlorobenzene, and mirex. Organochlorine residues analyzed at WATS included the list analyzed at MSCL plus aldrin, endosulfan I, endosulfan II, endosulfan sulfate, dicofol, heptachlor, methoxychlor, and tetradifon. DDT results are reported as total DDT which is the summation of the p,p'- and o,p'-homologs of DDT. Total chlordane is the summation of the compounds and by-products of chlordane that were analyzed. Results are reported in ppm wet weight unless otherwise stated. Detection limits are listed in Table 2 for WATS and incorporated into Tables 9 to 10 for MSCL.

# Results

# Metal Contaminants

Biotic samples collected in Elk Creek contained residue concentrations of all metals contaminants analyzed except arsenic, lead, and thallium, which were reported at levels below the detection limit (Table 3). Residue concentrations of selenium ranged from 0.90 ppm to 1.0 ppm in bullheads and 1.5 ppm in the carp collected. Mercury concentrations in bullheads ranged from 0.19 ppm to 0.44 ppm, while the level was 0.22 ppm in carp. Residue concentrations of copper in bullheads ranged from 3.76 to 7.86 ppm, and the concentration determined in carp was 3.99 ppm.

Arsenic, lead, and thallium were the only metal contaminants found at levels below the detection limit in biotic samples collected from Honeyhouse Creek (Table 4). The selenium residue concentrations found in turtle liver was 1.8 ppm and in bullheads ranged from 0.31 to 0.47 ppm. The turtle liver contained 0.60 ppm mercury and bullheads contained 0.10 to 0.11 ppm mercury. Copper concentrations ranged from 0.72 to 1.88 ppm in bullheads and was at 6.2 ppm in

Table 1. Detection limits of metal contaminants analyzed by the Environmental Trace Substances Research Center, Columbia, Missouri.

	Detection Limi	Detection Limits (Dry Weight)						
	Aluminum	0.4-0.5						
•	Arsenic	0.1						
	Beryllium	0.01						
	Cadmium	0.03-0.05						
	Chromium	0.1						
	Copper	0.02-0.03						
	Iron	0.02-0.1						
,	Lead	0.5-0.6						
	Manganese	0.03						
	Mercury	0.1						
	Nickel	0.2						
	Selenium	0.1						
	Thallium	0.5-0.6						
	Zinc	0.03-0.04						

Table 2. Detection limits for organic compounds analyzed by Weyerhaeuser Analytical and Testing Services, Takoma, Washington.

	Compound	Detection Limit	
<u></u>	Total DDT'	0.05	
	PCBs (total)	0.10	
	Aldrin	0.05-1.0	
	Dieldrin	0.05-1.0	
	Endrin	0.05-1.0	
	Endosulfan I	0.05-1.0	
	Endosulfan II	0.05-1.0	
	Endosulfan sulfate	0.05-1.0	
	Dicofol	0.05-1.0	
	Total Chlordane <sup>2</sup>		
	Heptachlor	0.05-1.0	
	Heptachlor epoxide	0.05-1.0	
	cis-Chlordane	0.05-1.0	
	trans-Chlordane	0.05-1.0	
	cis-Nonachlor	0.05-1.0	
	trans-Nonachlor	0.05-1.0	
	Oxychlordane	0.05-1.0	24. 33
	Methoxychlor	0.05-1.0	
	Tetradifon	0.05-1.0	
	Toxaphene	0.51	
	α-Benzene hexachloride (BHC)	0.05	
	β-BHC	0.05	
	Δ-BHC	0.05	
	γ-BHC	0.05	
	η-BhC Hexachlorobenzene	0.05	
	Mirex	0.05	

<sup>&#</sup>x27;Sum of p,p'- and o,p'-homologs of DDT.
'Sum of the components (indented compounds) which comprise chlordane.

Table 3. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in bullheads (*Ictalurus* sp.) and carp (*Cyprinus carpio*) collected from Elk Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

			Carp					
Compound	DW	WW	DW	WW	ĎW	WW	DW	WW
Aluminum	573.0	166	94.4	27.5	160	47.2	353	119
Arsenic	<0.1	<0.03	<0.1	<0.03	<0.1	<0.03	0.36	0.12
Beryllium	0.038	0.01	0.02	0.006	0.03	0.009	0.03	0.01
Cadmium	0.08	0.02	0.09	0.03	0.08	0.02	0.04	0.01
Chromium	2.2	0.64	3.7	1.1	2.1	0.62	2.1	0.71
Copper	7.86	2.27	3.76	1.1	4.41	1.3	3.99	1.34
Iron	371	98.5	129	37.5	154	45.4	208	70.1
Lead	<0.5	<0.14	<0.6	<0.17	<0.5	<0.15	<0.6	<0.2
Manganese	38.7	11.2	42.9	12.5	23.7	7.0	77.5	26.1
Mercury	0.44	0.13	0.37	0.11	0.19	0.19	0.22	0.07
Nickel	1.3	0.38	5.2	1.5	1.3	0.38	1.2	0.4
Selenium	0.90	0.26	0.98	0.29	1.0	0.3	1.5	0.51
Thallium	<0.5	<0.14	<0.6	<0.17	<0.5	<0.15	<0.6	<0.2
Zinc	60.3	17.4	61.2	7.8	63.0	18.6	64.4	21.7
% Moisture	71	.1		0.9	. 70	0.5		5.3

Table 4. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in bullheads (*Ictalurus* sp.) and a turtle collected from Honeyhouse Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

				Bulli	neads				<u>Turtle</u>	<u>Liver</u>
Compound	DW	WW	DW	WW	DW	WW	DW	WW	DW	WW
Aluminum	48.2	14.2	49.7	13.8	56.3	15.1	71.3	172	66.1	15.9
Arsenic	<0.1	<0.03	<0.1	<0.1	<0.1	<0.03	<0.1	<0.02	0.1	0.02
Beryllium	0.02	0.006	0.03	0.008	0.02	0.005	0.02	0.005	0.038	
Cadmium	0.06	0.02	0.08	0.02	0.07	0.02	0.13	0.03	1.3	0.31
Chromium	0.92	0.27	3.3	0.91	2.1	0.56	2.2	0.53	1.0	0.24
Copper	6.40	1.88	3.38	0.94	2.69	0.72	3.66	0.88	67.4	6.2
Iron	91.1	27.0	84.6	23.4	105	28.2	181	43.6	5620	1354
Lead	<0.5	<0.1	<0.5	<0.14	<0.5	<0.13	<0.5	<0.12	<0.5	<0.12
Manganese	37.9	11.1	41.0	11.4	43.2	11.6	39.7	9.57	5.6	1.3
Mercury	0.36	0.11	0.40	0.11	0.36	0.10	0.44	0.11	2.5	0.60
Nickel	0.66	0.19	2.2	0.61	1.3	0.35	1.5	0.36	1.6	0.39
Selenium	1.4	0.41	1.7	0.47	1.3	0.35	1.3	0.31	7.5	1.8
Thallium	<0.5	<0.1	<0.5	<0.14	<0.5	<0.13	<0.5	<0.12	<0.5	<0.12
Zinc	69.3	20.4	71.1	19.7	82.5	22.1	91.7	22.1	73.8	17.8
% Moisture		.6	72			.1	75	.9	75	5.9

turtle liver. Zinc residue concentrations ranged from 19.7 to 22.1 ppm in bullheads, and was 17.8 ppm in the turtle liver.

Metal concentrations in fish samples collected from Turkey Creek that were found at or less than the detection limit included arsenic, beryllium, cadmium, lead, and thallium (Table 5). Selenium concentrations ranged from 1.5 to 2.5 ppm. Mercury concentrations ranged from 0.37 to 0.64 ppm. Concentrations of chromium were found to be 0.75 to 5.4 ppm and copper to be 3.29 to 17.7 ppm.

Fish samples collected in Yellow Creek contained residue concentrations of all metals contaminants analyzed except arsenic, beryllium, lead, and thallium, which were reported at levels below the detection limit (Table 6). Selenium concentrations ranged from 1.2 to 2.4 ppm. Mercury concentrations ranged from 0.3 to 0.66 ppm, and copper was found in concentrations ranging from 95.9 to 245 ppm.

# Organochlorine Contaminants

Only two organochlorines were found in the samples collected from Elk Creek, dieldrin and methoxychlor (Table 7), but the concentrations were below the detection limit. Dieldrin residue concentrations ranged from 0.02 ppm to 0.04 ppm in bullheads and the residue concentration in carp was 0.03 ppm dieldrin (Table 7). Methoxychlor residue concentrations were at 0.01 ppm and 0.02 ppm in bullheads and 0.02 ppm in carp (Table 7).

Several organochlorines were detected in the samples collected in Honeyhouse Creek, including endrin, heptachlor epoxide, methoxychlor, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, and oxychlordane (Table 8). Bullheads collected contained residue concentrations of dieldrin at 0.09 ppm, 0.34 ppm, 0.09 ppm and 0.49 ppm (Table 8). The fat analyzed from the turtle collected had a dieldrin residue concentration of 1.5 ppm. Total DDT was detected in three of the bullheads, 0.07 ppm, 0.01 ppm and 0.11 ppm, respectively (Table 8).

Heptachlor epoxide, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, and total DDT were detected in carp and bigmouth buffalo collected from Turkey Creek (Table 9). Dieldrin residue concentrations ranged from 0.07 ppm to 0.21 ppm (Table 9). Toxaphene residue concentrations found were at 0.12 ppm and 0.61 ppm in carp, and 0.23 ppm in bigmouth buffalo (Table 9).

Organochlorines detected in samples collected in Yellow Creek include heptachlor epoxide, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, and total DDT (Table 10). Residue concentrations of dieldrin ranged from 0.05 to 0.11 ppm in carp and 0.06 ppm in quillback collected. Toxaphene concentrations were 0.05 ppm, 0.16 ppm, and 0.24 ppm in carp, and 0.14 ppm in quillback.

Table 5. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in a bigmouth buffalo (*Ictiobus cyprinellus* sp.) and carp (*Cyprinus carpio*) collected from Turkey Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

			Ca:		Bigmouth Buffalo			
Compound	DW	WW	DW	WW	DW	WW	DW	ww
Aluminum	22	7	14	4	59.7	17	81.6	21
Arsenic	<0.1	<0.03	0.2	0.05	0.2	0.06	0.3	0.08
Beryllium	<0.01	<0.003	<0.01	<0.002	<0.01	<0.003	<0.01	<0.003
Cadmium	0.1	0.03	0.17	0.04	0.1	0.02	0.1	0.03
Chromium	0.75	0.25	5.4	1.4	0.9	0.26	2.0	0.5
Copper	4.16	1.4	17.7	4.6	3.71	1.1	3.29	0.8
Iron	92.2	31	126	33	147	43	133	34
Lead	<0.4	<0.1	<0.5	<0.1	<0.5	<0.1	<0.5	<0.1
Manganese	32.5	10.8	29	8	51.3	15	38.2	9.6
Mercury	0.64	0.2	0.37	0.1	0.37	0.1	0.56	0.1
Nickel	0.3	0.1	0.62	0.2	0.62	0.2	0.3	0.08
Selenium	1.5	0.5	2.2	0.6	2.5	0.7	1.6	0.4
Thallium	<0.5	<0.2	<0.6	<0.2	<0.6	<0.2	<0.6	<0.2
Zinc	250	83	375	98	219	64	72.5	18
% Moisture	66	. 9	73.	8	70.8	3	74	. 8

Table 6. Residue concentrations of metal contaminants (part per million dry weight (DW) and wet weight (WW)) found in a quillback (Carpiodes cyprinus sp.) and carp (Cyprinus carpio) collected from Yellow Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by the Environmental Trace Substances Research Center, Columbia, Missouri.

			Ca	Quillback_				
Compound	DW	ww	DW	WW	DW .	ww	DW	ww
Aluminum	258	86	23	7	74.1	22	125	35
Arsenic	<0.1	<0.03	0.1	0.03	<0.1	<0.03	<0.1	<0.03
Beryllium	0.02	0.007	<0.01	<0.02	<0.01	<0.003	<0.01	<0.003
Cadmium	0.35	0.1	0.1	0.03	0.1	0.03	<0.07	<0.02
Chromium	0.4	0.1	0.63	0.2	1.0	0.3	1.5	0.4
Copper	3.62	1.2	3.57	1.1	3.55	1.1	2.43	0.7
Iron	245	82	95.9	28	139	42	195	55
Lead	<0.5	<0.2	<0.4	<0.1	<0.4	<0.1	<0.5	<0.1
Manganese	21.3	7.1	15.3	4.5	24.7	7.5	39.7	11.2
Mercury	0.3	0.1	0.66	0.2	0.44	0.1	0.58	0.2
Nickel	0.4	0.1	0.36	0.1	0.38	0.12	5.3	1.5
Selenium	2.0	0.7	1.9	0.6	1.2	0.4	2.4	0.7
Thallium	<0.5	<0.2	<0.5	<0.1	<0.5	<0.2	<0.6	<0.2
Zinc	288	96	373	111	224	68	65.2	18
% Moisture	66	.5	70.		69.	7	71	. 8

Table 7. Residue concentrations of organic contaminants (part per million wet weight) found in bullheads (*Ictalurus* sp.) and carp (*Cyprinus carpio*) collected from Elk Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by Weyerhaeuser Analytical and Testing Services, Takoma, Washington.

Compound	I	Bullhead	is	Carp
Total DDT <sup>1</sup>	ND²	ND	ND	ND
PCBs (total)	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND
Dieldrin	0.02	0.03	0.04	0.03
Endrin	ND	ND	ND	ND
Endosulfan I	ND	ND	ИD	ND
Endosulfan II	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND
Dicofol	ND	ND	ND	ND
Total Chlordane <sup>3</sup>	(ND)	(ND)	(ND)	(ND)
Heptachlor	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	ND
cis-Chlordane	ND	ND	ND	ND
trans-Chlordane	ND	ND	ND	ND
cis-Nonachlor	ND	ND	ND	ND
trans-Nonachlor	ND	ND	ND	ND
Oxychlordane	ND	ND	ND	ND
Methoxychlor	0.02	0.01	0.01	0.02
Tetradifon	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND
α-Benzene hexachlorid				
(BHC)	ND	ND	ND	ND
β-BHC	ND	ND	ND	ND
<b>Δ</b> - BHC	ND	ND	ND	ND
γ-BHC	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Mirex	ND	ND	ND	ND
* Moisture	70.3	71.7	70.3	68.2
% Moisture % Lipid	1.6	1.2	3.7	3.2

Sum of p,p'- and o,p'-homologs of DDT.

<sup>&</sup>lt;sup>2</sup>ND indicates at or below the detection limit.

<sup>&</sup>lt;sup>3</sup>Sum of the components (indented compounds) which comprise chlordane.

Table 8. Residue concentrations of organic contaminants (part per million wet weight) found in bullheads (*Ictalurus* sp.) and a turtle collected from Honeyhouse Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by Weyerhaeuser Analytical and Testing Services, Takoma, Washington.

					Tur	tle
Compound		Bull	lheads		Liver	Fat
Total DDT <sup>1</sup>	ND²	0.07	0.01	0.11	ND	ND
PCBs (total)	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND
Dieldrin	0.49	0.09	0.39	0.34	ND	1.50
Endrin	ND	ND	ND	0.01	0.09	0.01
Endosulfan I	ND	ND	ND	ND	ND	ND
Endosulfan II	ND	ND	ŃD	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND
Dicofol	ND	ND	ND	ND	ND	ND
Total Chlordane <sup>3</sup>	(0.33)	(0.17)	(0, 29)	(0.33)	(0.09)	(1.17)
Heptachlor	ND	ND	ND	ND	ND	ND
Heptachlor epoxide	0.18	0.02	0.14	0.13	0.05	0.68
cis-Chlordane	0.02	0.02	0.03	0.04	ND	ND
<i>trans-</i> Chlordane	0.06	0.03	0.06	0.08	ND	0.02
cis-Nonachlor	ND	ND	ND	ND	ND	ND
trans-Nonachlor	0.03	0.08	0.03	0.04	0.01	0.25
Oxychlordane	0.02	ND	0.02	0.02	0.01	0.19
Methoxychlor	0.02	0.02	0.01	0.02	0.02	0.03
Tetradifon	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND
α-Benzene hexachloride						
(BHC)	ND	ND	ND	ND	ND	ND
β-BHC	ND	ND	ND	ND	ND	0.01
Δ-BHC	ND	ND	ND	ND	ND	ND
γ-BHC	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND	ND
% Moisture	70.7	72.2	72.4	75.8	76.4	78.3
% Lipid	2.4	0.4	2.3	1.6	7.1	19.5

<sup>&#</sup>x27;Sum of p,p'- and o,p'-homologs of DDT.

 $<sup>^2\</sup>mathrm{ND}$  indicates at or below the detection limit. The detection limit for all compounds was 0.05 ppm, except toxaphene, which was 0.50 ppm.

<sup>&</sup>lt;sup>3</sup>Sum of the components (indented compounds) which comprise chlordane.

Table 9. Residue concentrationss of organic contaminants (part per million wet weight) found in a bigmouth buffalo (*Ictiobus cyprinellus*) and carp (*Cyprinus carpio*) collected from Turkey Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by Mississippi State Chemical Laboratory, Mississippi State, Mississippi.

Compound		Carp		Bigmouth Buffalo
Total DDT <sup>1</sup>	0.09	0.03	0.02	0.03
PCBs (total)	$ND^2$	ND	ND	ND
Dieldrin	0.21	0.07	0.09	0.19
Endrin	ND	ND	ND	ND
Total Chlordane <sup>3</sup>	(0.36)	(0.1)	(0.13)	(0.15)
Heptachlor epoxide	0.10	0.04	0.04	0.04
cis-Chlordane	0.05	0.01	0.02	0.02
<i>trans-</i> Chlordane	0.06	0.02	0.03	0.03
cis-Nonachlor	0.05	ND	ND	0.02
trans-Nonachlor	0.07	0.02	0.03	0.03
Oxychlordane	0.03	0.01	0.01	0.01
Toxaphene	0.61	0.12	0.12	0.23
α-Benzene hexachloride				
(BHC)	ND	ND	ND	ND
β-BHC	ND	ND	ND	ND
Δ-BHC	ND	ND	ND	ND
γ-BHC	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Mirex	ND	ND	ND	ND
% Moisture	65.2	71.6	70.2	74.0
% Lipid	12.2	4.8	5.8	3.7

<sup>&</sup>lt;sup>1</sup>Sum of p,p'- and o,p'-homologs of DDT.

<sup>&</sup>lt;sup>2</sup>ND indicates none detected. Detection limits for organochlorines was 0.01 ppm, and 0.05 ppm for toxaphene and PCBs.

<sup>&</sup>lt;sup>3</sup>Sum of the components (indented compounds) which comprise chlordane.

Table 10. Residue concentrations of organic contaminants (part per million wet weight) found in a quillback (*Carpiodes cyprinus*) and carp (*Cyprinus carpio*) collected from Yellow Creek on Swan Lake National Wildlife Refuge, Chariton County, Missouri. Analyses were conducted by Mississippi State Chemical Laboratory, Mississippi State, Mississippi.

Compound		Carp		Quillback
Total DDT <sup>1</sup>	0.05	0.01	0.03	0.04
PCBs (total)	$ND^2$	ND	ND	ND
Dieldrin	0.11	0.05	0.09	0.06
Endrin	ND	ND	ND	ND
Total Chlordane <sup>3</sup>	(0.23)	(0.14)	(0.11)	(0.14)
HeptachÍor epoxide	0.06	0.03	0.04	0.02
cis-Chlordane	0.04	0.02	0.02	0.03
<i>trans-</i> Chlordane	0.04	0.06	0.02	0.04
cis-Nonachlor	0.03	0.01	ND	ND
<i>trans-</i> Nonachlor	0.04	0.01	0.02	0.04
Oxychlordane	0.02	0.01	0.01	0.01
Toxaphene	0.24	0.05	0.16	0.14
α-Benzene hexachloride				
(BHC)	ND	ND	ND	ND
β-BHC	ND	ND	ND	ND
Δ-BHC	ND	ND	ND	ND
γ-BHC	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Mirex	ND	ND	ND	ND
% Moisture	66.4	69.8	69.8	74.0
% Lipid	11.7	7.3	8.9	4.2

<sup>&</sup>lt;sup>1</sup>Sum of p,p'- and o,p'-homologs of DDT.

3Sum of the components (indented compounds) which comprise chlordane.

<sup>&</sup>lt;sup>2</sup>ND indicates none detected. Detection limits for organochlorines was 0.01 ppm, and 0.05 ppm for toxaphene and PCBs.

# Discussion

Numerous tests have been conducted on the sensitivity of different species exposed to contaminants in water, but information is lacking on the concentrations of contaminants in animal tissue that will directly harm the organism, or cause stress, thus exposing the animal as easier prey. Information also is lacking for concentrations that will harm predators which may consume a contaminated organism. There are only a few established action and alert levels for tolerable tissue concentrations of contaminants that may protect fish and wildlife resources, but there are no uniformly accepted standards (Irwin 1988).

When comparing contamination levels, one has to realize that some data are based on fillet (edible to humans) samples and some on whole-body samples. Also, different species and tissue types have different abilities in accumulating contaminants (e.g., fatty tissues accumulate organic contaminants, muscle tissues accumulate few contaminants)(Irwin 1988). Therefore, the data presented in this report have been conservatively compared to that in scientific literature, mainly from the Service's National Contaminant Biomonitoring Program (NCBP)(Schmitt and Brumbaugh 1990, Schmitt et al. 1990). Only those contaminants that were at concentrations above the detection limits are discussed below.

#### Metal Contaminants

#### Aluminum

Aluminum is the third most abundant element in the earth's crust, but it does not occur as a pure metal in nature. It's solubility is dependent on pH, and it will dissolve and enter into the aquatic environment. In surface waters, aluminum exists as an aluminate anion, molecular aluminum hydroxide, and as an aluminum cation (Burrows 1977). Sources of aluminum in the environment include wastewater treatment plant effluent, industrial effluent, and mining activities.

When surface waters are at a low pH, aluminum is more readily available to aquatic species and can be harmful. In acidic lakes, aluminum may cause reduction in fish survival and undesirable effects on growth rates (Howells et al. 1983). Aluminum is known to affect amphibians by reducing their hatching success (Clark and Hall 1985). In birds, aluminum may reduce prey availability, reduce clutch sizes and cause them to produce defective eggshells (Nyholm 1981, Havas 1986).

No reference data could be found to determine if residue concentrations of aluminum found in the fish collected at SLNWR could cause any adverse effects to fish populations or predators. Concentrations of aluminum were not measured in the fish samples collected for the NCBP (Schmitt and Brumbaugh 1990). Aluminum was analyzed in fish collected at Clarence Cannon National Wildlife Refuge and in comparison, SLNWR had the highest residue level of aluminum in a bullhead collected from Elk Creek.

## Chromium

Chromium is a naturally occurring metal in the earth's crust. In the environment it is found in three major states; chromium (III) which occurs naturally, chromium (0), and chromium (VI), both of which are produced by industrial processes. Chromium is an essential element used in the process of metabolism of glucose, cholesterol, and fat (SRC 1989). Chromium also can be found in small quantities in the RNA of a few organisms (Moore and Ramamoorthy 1984a). Only chromium (VI) is known to be toxic (Faust and Aly 1981) and is a probable cancer-causing agent (SRC 1989).

Various chromium compounds are used for chrome plating, manufacture of pigments, leather tanning, wood treatment, water treatment, corrosion inhibitors, laundry chemicals, and in animal glue manufacture. Chromium is used for making steel and other metal alloys. Chromium as mineral chromite is used to make bricks for metallurgical furnaces.

Chromium is released into the environment in large amounts by human activity. Atmospheric chromium contamination results from coal and oil combustion, steel production, chemical manufacture, chrome plating, and cooling tower emissions (Moore and Ramamoorthy 1984a, SRC 1989). The particulates may be deposited close to the emission site by precipitation or be windblown over long distances. Surface water chromium contamination can originate from municipal and industrial releases and from chromium-bearing sediments from storm runoff from urban areas and drainage of eroded soils (Faust and Aly 1981, Moore and Ramamoorthy 1984a). Chromium contamination of the land may be due to improper disposal of solid wastes from chromate manufacture and copying machine toner powder waste (SRC 1989).

There is a wide range of chromium toxicity to aquatic biota depending on the influence of many biotic and abiotic factors. These factors include species, life stage, temperature, pH, chromium valence, hardness, and salinity (Faust and Aly 1981, Eisler 1986). Eisler (1986) reported  $LC_{50}$  (96 h) values for sensitive freshwater fish between 0.445 and 2.0 ppm chromium (VI). Faust and Aly (1981) listed  $LC_{50}$  (96 h) values and safe concentrations for chromium (VI) for fathead minnows in hard water to be 33 and 1 ppm, respectively, for brook trout in soft water to be 50 and 0.6 ppm, and for rainbow trout in soft water to be 69 and 0.3 ppm.

Chromium is mutagenic, carcinogenic, and teratogenic under laboratory conditions (Eisler 1986). Information for wild species is limited. Chronic effects of chromium contamination include decreased growth and body size, reduced rate of reproduction, and survival of progeny (Moore and Ramamoorthy 1984a, Eisler 1986). Chromium does not bioaccumulate and does not concentrate in specific tissues as other metals do (Moore and Ramamoorthy 1984a).

Eisler (1986:44) states "the significance of Cr [chromium] residues is unclear, but available evidence suggests that organs and tissues of fish and wildlife that contain >4.0 mg total Cr/kg [ppm] dry weight should be viewed as presumptive evidence of Cr contamination". Two samples from SLNWR, bullheads from Honeyhouse Creek (3.3 ppm dry weight) and Elk Creek (3.7 ppm dry weight), approach the chromium residue concentration of concern reported by Eisler, and

one carp sample from Turkey Creek (5.4 ppm dry weight) was in excess. Therefore, we conclude that chromium contamination is a possibility on SLNWR.

# Copper

Copper, an essential element in life processes, is a reddish metal that occurs naturally in the air, water, sediment, rock, and soil (SRC 1990). Copper is used in a wide range of products because of its physical properties including high thermal and electrical conductivity, low corrosion rate, alloying ability, and appearance (Moore and Ramamoorthy 1984a, SRC 1990). Copper is extensively mined and processed in the United States and is used in electrical wiring, sheet metal, pipe, and the U.S. coinage. Copper is mixed with other metals to produce alloys such as bronze, brass, gun metal, and sterling silver. Copper compounds are used in water treatment, and preservatives for wood, leather, and fabrics.

As a natural constituent in soil, copper is naturally discharged into the environment by wind-blown dust and runoff from the natural weathering of rock and soil (Moore and Ramamoorthy 1984a, SRC 1990). The major discharges of copper are anthropogenic sources such as production of nonferrous metals, wood combustion, iron and steel production, waste incineration, nonferrous metal mining, phosphate fertilizer manufacture, and domestic wastewater discharges (Moore and Ramamoorthy 1984a, SRC 1990).

Copper and copper compounds are priority pollutants as defined by the U.S. Environmental Protection Agency (EPA)(see 40 CFR 401.15). EPA has determined that the level of copper in surface waters should not exceed 1 ppm for protection of human health. This limit takes into account ingestion of copper through water and contaminated aquatic organisms (SRC 1990). Copper concentrations in relatively uncontaminated surface waters range from 0.0005 to 0.001 ppm, and can increase to  $\geq 0.002$  ppm in urban areas (Moore and Ramamoorthy 1984a). Sediment concentrations of copper tend to be high because the metal is absorbed to the sediments rapidly depending on the type of clay/sediment, pH, and competing cations (Moore and Ramamoorthy 1984a).

The toxicity of copper to fish is usually higher than any other metal except mercury (Moore and Ramamoorthy 1984a). The  $LC_{50}$  ranges from 0.017 to 1.0 ppm copper, with acute toxicity depending on water hardness and different susceptibilities among species. Chronic toxicity of copper can reduce survival, growth, and rate of reproduction in fish (Moore and Ramamoorthy 1984a).

Residue concentrations of copper in invertebrates collected in polluted surface waters range from 5 to 200 ppm in soft tissues (Moore and Ramamoorthy 1984a). There is no accumulation of copper through the food chain, but contaminated food is probably the most important source of the metal when compared to water (Moore and Ramamoorthy 1984a). Muscle tissue residues in fish collected from metal-contaminated lakes near Sudbury, Ontario ranged from 0.5 to 1.4 ppm copper (Bradley and Morris 1986). While muscle tissue residue concentrations of copper tend to be low, high concentrations may be found in livers of fish (Moore and Ramamoorthy 1984a, SRC 1990). Thus, liver tissue is a better indicator of copper contamination than whole fish samples.

All samples collected from the SLNWR contained copper residue concentrations greater than the NCBP geometric mean of 0.65 ppm wet weight (Schmitt and Brumbaugh 1990). Eleven of the sixteen fish sample concentrations were higher than the 85th percentile concentration of 1.0 ppm wet weight copper. None of the sample concentrations exceeded the maximum of 23.1 ppm wet weight copper.

However, copper concentrations found in fish samples from SLNWR are in the same range and in some cases greater than concentrations in fish collected from metal-contaminated lakes near Sudbury, Ontario. A direct comparison is difficult since only muscle tissue of fish was analyzed by Bradley and Morris versus whole-body samples from SLNWR. Heavy metals tend to accumulate in the liver and those residue concentrations would not be evidenced in muscle tissue samples. There may be a copper contamination problem at SLNWR as well.

#### Iron

Although iron is the second most abundant metal and fourth among all elements in the earth's crust, pure iron is not common in the natural environment (Nebergall  $et\ al.\ 1980$ ). Iron can be found in almost all rocks, minerals, soils, plants, and animals. Iron is an essential element in most animals, present in the hemoglobin of blood which acts as an oxygen carrier.

Iron-bearing ores are the common form of iron found in the environment, including hematite, magnetite, limonite, lodestone, taconite, and pyrite. Steels, such as carbon steel and stainless steel, are produced using iron and other metal alloys.

Iron is corroded (e.g., oxidizes) when exposed to air and water. The resulting ions may constitute pollutants in surface waters (McKee and Wolf 1963). Other sources of iron pollutants are iron-bearing industrial wastes such as those from pickling operations and acid-mine drainage (McKee and Wolf 1963).

Concentrations of iron are purposely limited in public drinking water because of the objectionable taste, staining of plumbing fixtures, spotting of laundry, and accumulation in pipes (NAS/NAE 1972).

Iron salts (e.g. ferric chloride, ferrous sulfate) dissociate in water and the resulting ferric or ferrous ions combine with hydroxyl ions and precipitate. The addition of iron salts in surface water that is not strongly buffered may lower the pH to a toxic level (McKee and Wolf 1963). The precipitated iron hydroxides may deposit on the gills of fish causing irritation and blockage of respiratory channels (McKee and Wolf 1963). Also, heavy deposits of ferric hydroxide can smother fish eggs.

Iron was not analyzed in the fish collected for the NCBP (Schmitt and Brumbaugh 1990). Iron concentrations in edible tissues of fish collected from streams contaminated by lead mining ranged from 0.3 to 25.0 ppm wet weight (Schmitt and Finger 1987). Residue concentrations of iron (23.4 to 98.5 ppm wet weight) from SLNWR samples were greater than those reported by Schmitt and Finger (1987). This may be due to the type of sample analyzed, whole fish versus edible tissue. Heavy metals tend to accumulate in the liver and those

residue concentrations would not be evidenced in edible tissue samples. No reference data could be found to determine if residue concentrations of iron found in the fish collected at SLNWR could cause any adverse effects to the fish population or predators.

# Manganese

In its elemental form, manganese is a brittle, gray-white metal. While elemental manganese is not in the natural environment, its compounds are very common. Manganese ores are used in alloy to make steels for rails, safes, and heavy machinery or instruments for making electrical measurements (Nebergall et al. 1980). Manganese salts are used in dry-cell batteries, glass-making and ceramics, manufacture of paints and varnishes, inks and dyes, matches and fireworks, in disinfectants, deodorant and germicides (McKee and Wolf 1963, Nebergall et al. 1980). Manganese also is a required trace element for plants and animals (NAS/NAE 1972).

Manganese in surface waters can result from leaching of surrounding soils, air pollution deposition from power plants, sewage treatment plant effluents, and leachates from municipal landfills (NAS/NAE 1972, Irwin 1988). Manganese compounds are only slightly soluble in water, so manganous and manganic ions usually are in low concentrations, <1 ppm, in surface waters (McKee and Wolf 1963, NAS/NAE 1972).

Concentrations of manganese are kept low (<0.05 ppm) in public water supplies. Like iron, manganese affects taste, stains plumbing fixtures, spots laundry, and accumulates in pipes (NAS/NAE 1972).

The toxicity of manganese to fish depends on several factors such as species, type of manganese compound, or presence of other metals (McKee and Wolf 1963). The lethal concentration of manganese for stickleback was 40 ppm in water with the toxic action being slow (from NAS/NAE 1972). Carp and trout have been shown to tolerate 15 ppm manganese during seven days of exposure (from NAS/NAE 1972).

No reference data could be found to determine if residue concentrations of manganese found in the fish collected at SLNWR could cause any adverse effects to fish populations or predators. Manganese residue concentrations in edible portions of fish collected from streams contaminated by lead mining ranged from 0.08 to 1.90 ppm wet weight (Schmitt and Finger 1987). Whole fish residue concentrations of manganese (4.5 to 26.1 ppm wet weight) in SLNWR samples were much higher. Manganese is known to accumulate in bone, skin, and scales in orders of magnitude higher than muscle (from Schmitt and Finger 1987). Thus, the difference in manganese residue concentrations can be attributed to the difference in fish samples analyzed (i.e., whole body versus edible tissue).

## Mercury

Mercury is the only metal found in liquid form at normal ambient temperatures and is distributed throughout the environment. The largest industrial use for mercury is in electrolytic preparations of chlorine and caustic soda (Faust

and Aly 1981). Mercury also is used in thermometers, barometers, manometers, batteries, high-intensity street lamps, fluorescent lights, insecticides, fungicides, bactericides, pharmaceuticals, dental preparation, and employed as a shield against atomic radiation (Faust and Aly 1981, Moore and Ramamoorthy 1984a, Clement Associates 1989a).

The Study Group on Mercury Hazards (1971:26) states that "decontamination through natural processes is extremely slow and, considering the large volumes of mercury contained in some bottom sediments, it is quite conceivable that some waters will remain contaminated for 100 years or more". Mercury is constantly released into the air from ore deposits and soil surfaces because it is highly volatile (Moore and Ramamoorthy 1984a). Anthropogenic sources contribute more mercury into the environment than natural sources. These sources include burning of fossil fuels, smelting operations of mercury-containing ores, operation of chloralkali plants, incineration of municipal sludges, and disposal of batteries and fluorescent lamps (Faust and Aly 1981, Moore and Ramamoorthy 1984a, from Eisler 1987).

Toxic concentrations of mercury range from 0.15 to 0.20 ppm (96 h  $LC_{50}$ ) for juvenile rainbow trout and 0.03 ppm (10 d  $LC_{50}$ ) for channel catfish embryolarvae (from Eisler 1987). Mercury as mercuric chloride was lethal to bivalve larvae at 0.027 ppm (from NAS/NAE 1972). Mercury as mercuric sulfate caused severe deformities in developing salmon (Oncorhynchus nerka and O. gorbuscha) at concentrations exceeding 0.003 ppm mercury. Flaring of gill covers, loss of equilibrium and sluggishness are signs of acute mercury poisoning (from Eisler 1987).

Chronic mercury poisoning causes emaciation, brain lesions, cataracts, inability to capture food, and abnormal motor coordination in different fish species (from Eisler 1987). Sublethal poisoning in fish also can cause inhibition of enzymes and protein synthesis in liver, kidney, and brain, reduction in sperm viability and survival of second generation fry, and reduction in fin regeneration time (Moore and Ramamoorthy 1984a). These symptoms reduce the ability of fish to survive in the natural environment.

Mercury has no known normal metabolic function in living organisms. The majority of the mercury found in fish is methylmercury (from Faust and Aly 1981, Moore and Ramamoorthy 1984a). Faust and Aly (1981) stated that alkylmercurials cumulate in the food chain and are concentrated by aquatic organisms. In fish from relatively unpolluted sites, the average concentrations of mercury is less than 0.2 ppm (Clement Associates 1989a).

In a review of the literature, Eisler (1987) found that concentrations of mercury in biotic samples collected from areas not directly impacted by man were usually <1.0 ppm fresh weight. However, samples collected in the vicinity of point and nonpoint sources of mercury contained concentrations exceeding 1.0 ppm fresh weight, sometimes significantly. Muscle tissue of channel catfish (*Ictalurus punctatus*) collected in Lake Erie had mercury residue concentrations of 0.3 to 1.8 ppm fresh weight; from Lake St. Clair, 0.5 to 2.0 ppm fresh weight; and from Texas, 0.2 to 2.5 ppm fresh weight (from Eisler 1987).

Common carp and bluegills collected from the upper Mississippi River were analyzed as whole body samples; and liver samples also were analyzed from the carp. Mercury concentrations in the whole fish samples ranged from 0.179 to 1.43 ppm dry weight in carp and 0.158 to 0.325 ppm dry weight in bluegill (Weiner et al. 1984). Carp liver samples ranged from 0.092 to 7.91 ppm dry weight mercury (Weiner et al. 1984).

Mercury concentrations in fish collected from the NCBP had a geometric mean of 0.10 ppm wet weight, with a maximum concentration of 0.37 ppm wet weight in a largemouth bass from Pee Dee River, South Carolina (Schmitt and Brumbaugh 1990). Concentrations of mercury in individual fish depends on the waterbody in which it lives, species, and age and size of the fish (Murray 1978).

Only four of the 16 fish samples from SLNWR were slightly greater than the 85th percentile of 0.17 ppm wet weight mercury determined for the NCBP (Schmitt and Brumbaugh 1990). Of those four, none exceeded the maximum level of 0.37 ppm wet weight reported above. Also, concentrations of mercury found in SLNWR fish were at the lower end of ranges of concentrations found in fish from areas of potential mercury contamination reported above. There apparently is not a mercury contamination problem in the fish on SLNWR.

#### Nickel 1

Nickel is not found in its elemental form in nature. It is present in many ores, minerals, and soils. Nickel has good thermal and electrical conductivity and is highly magnetic. Nickel is used in coinage, electroplating and in more than 3,000 different alloys such as stainless steel and cast iron. The different alloys are used in instruments for electrical transmission and reproduction of sound, electrical heating units, industrial equipment, manufacture of automobiles, heavy machinery and armaments, magnetic components in electrical equipment, nickel cadmium batteries, solar energy equipment, and dyes in ceramics and fabrics (NAS/NAE 1972, Nebergall et al. 1980, Moore and Ramamoorthy 1984a).

Surface water nickel contamination may result from eroded soil particles, industrial applications, fertilizer production, mine wastes and deposition from the atmosphere due to automobile combustion, waste incineration, and wood and coal combustion (NAS/NAE 1972, Moore and Ramamoorthy 1984a).

Nickel ions can be toxic depending on species, water hardness, and synergism with other metallic ions (NAS/NAE 1972). Even though nickel is toxic, it is one of the least toxic of the heavy metals. The  $LC_{50}$  (48-96 h) for invertebrates ranges from 0.5 to 20 ppm nickel (Moore and Ramamoorthy 1984a). The  $LC_{50}$  (96 h) for fathead minnows (*Pimephalas promelas*) ranges from 5 ppm nickel in soft water to 43 ppm nickel in hard water (NAS/NAE 1972). The lethal limit of nickel for sticklebacks has been reported at 0.8 ppm (from McKee and Wolf 1963). Moore and Ramamoorthy (1984a) reported  $LC_{50}$ s (48-96 h) for adult fish ranging from 5 to 100 ppm nickel, with lower values reported for immature stages. Chronic effects have not been investigated fully, although there may be a reduction in fecundity and egg survival in fish.

Nickel contamination in invertebrates may occur at site specific points (Moore and Ramamoorthy 1984a). Nickel tends to accumulate in tissues with high metabolic activity, not in muscle tissue. Residue concentrations also vary seasonally due to reproductive activities and changing water temperature (Moore and Ramamoorthy 1984a). Moore and Ramamoorthy (1984a:171) suggest that "biomonitoring and impact assessment programs should not be based on muscle residue data".

Data on residue concentrations of nickel in fish is limited. Concentrations in fish collected from lakes and rivers near Sudbury, Ontario, an area heavily contaminated with metals, ranged from 9.5 to 13.8 ppm nickel wet weight (Hutchinson et al. 1975) Nickel residue concentrations in fish from other industrialized areas of the world seldom exceed 1 ppm wet weight.

Nickel concentrations in the fish collected from SLNWR are well below the concentrations reported for contaminated areas. Nickel was not measured in the fish collected for the NCBP (Schmitt and Brumbaugh 1990). In comparison to other sites sampled in Missouri, Clarence Cannon NWR had the highest maximum residue concentration of nickel (23.8 ppm dry weight). There does not seem to be a nickel contamination problem on SLNWR.

## Selenium

Selenium, an essential element to living organisms, is naturally occurring and widely, but unevenly distributed. Selenium is most commonly found in sedimentary rock. There are no significant deposits of selenium to mine; therefore, the majority of selenium used is produced from copper refinery slimes. The element selenium is used for photoelectric cells, xerographic copying machines, in the manufacture of glass and ceramics, in pigments to color plastics, paints and enamels, and in agriculture as a prevention of selenium deficiency in livestock and poultry (NAS/NAE 1972, Faust and Aly 1981, Clement Associates, Inc. 1989).

The weathering of natural rock is the major environmental source of selenium. Anthropogenic activities which contribute to selenium concentrations are the combustion of coal, coal fly ash, mining and milling operations, and selenium refining factories (Faust and Aly 1981, Clement Associates, Inc. 1989).

Dietary selenium is essential for living organisms; however, selenium in excess is toxic and can cause death (NAS/NAE 1972). Goldfish tested in softwater with pH ranging from 6.4 to 7.3 survived 10 ppm sodium selenate for only 98 to 144 h. (from NAS/NAE 1972). In a review of the literature, Eisler (1985) listed 96 h  $LC_{50}$ s for selenium contamination to various species, including the common carp at 35 ppm, mosquitofish at 12.6 ppm, channel catfish at 13.6 ppm, bluegill at 28.5 ppm, and rainbow trout ranging from 4.2 to 12.5 ppm. Signs of selenium poisoning in fish include, but are not limited to, loss of equilibrium, lethargy, muscle spasms, protruding eyes, and swollen abdomen (from Eisler 1985).

Sublethal effects of selenium were noted in green sunfish from a North Carolina lake contaminated with selenium from fly-ash wastes. Reproduction failed and the population decreased (Sorensen *et al.* 1984). Other noted

sublethal effects are growth reduction of green algae and rainbow trout fry, shifts in species composition of algal communities, and avoidance response in goldfish (Eisler 1985).

Selenium is accumulated through the food chain and is modified by water temperature, age of the organisms, mode of administration (Eisler 1985) and species of fish (Faust and Aly 1981). Selenium concentrations were higher in the kidney and liver than muscle tissue in carp (Sato et al. 1980). Concentrations of selenium in whole carp and bluegill from the upper Mississippi River ranged from 0.7 to 1.4 ppm dry weight; livers of carp contained 2.2 to 5.2 ppm dry weight (Wiener et al. 1984). Whole fish samples collected nationwide for the NCBP contained a geometric mean of 0.42 ppm wet weight selenium, with the highest level of 2.3 ppm wet weight from a carp collected in the Colorado River in Arizona (Schmitt and Brumbaugh 1990).

Seven of the 17 samples collected at SLNWR were only slightly higher than the NCBP geometric mean (Schmitt and Brumbaugh 1990). All of the fish samples were below the 85th percentile of 0.73 ppm wet weight selenium. There does not seem to be a selenium contamination problem at SLNWR.

#### Zinc

Rocks and ores containing zinc are mined and refined into pure zinc. The pure zinc is then used for galvanizing, in the production of noncorrosive alloys, brass, U.S. coinage, and for electrical purposes. Zinc salts are used in paint pigments, pharmaceuticals, cosmetics and insecticides.

Zinc compounds are found naturally in the air, water, soil, and all living organisms. Anthropogenic sources, which contribute 96% of the zinc discharged into the environment, include non-ferrous metal production, waste incineration, electroplating, drainage from active and inactive mining operations, domestic and industrial sewage effluents, combustion of fossil fuels, road surface runoff, and erosion of agricultural soils (Moore and Ramamoorthy 1984a, Clement Associates 1989c, from Eisler 1993).

Zinc is an essential element for living organisms, but in excess zinc can be toxic. The susceptibility of fish to zinc contamination depends on species, age, and health of the fish, water hardness, pH, and temperature (McKee and Wolf 1963, NAS/NAE 1972, Moore and Ramamoorthy 1984a), In an overview of the literature, Moore and Ramamoorthy (1984) found that the  $LC_{50}$  (48-96 h) for fish ranged from 0.5 to 5.0 ppm zinc, with an extension of the range from 0.09 to >100 ppm zinc due to physio-chemical and biological factors. The toxic action of zinc is thought to be caused through formation of insoluble compounds within the mucous that covers the gills, damage to the gill epithelium, or possibly as an internal poison (from McKee and Wolf 1963, Moore and Ramamoorthy 1984a).

Fish exposed to sublethal concentrations of zinc exhibit reproductive impairment, significant alterations in blood and serum chemistry, cholesterol, RNA, and proteins (from Eisler 1993), decrease in growth, maximum size and fecundity, and alteration in schooling and reproductive behaviors (Moore and Ramamoorthy 1984a).

Zinc residue concentrations in fish tissue are elevated at point sources and decrease further away from the source (from Eisler 1993). Zinc is obtained by organisms through their diet (Eisler 1993). In a review of the literature, Moore and Ramamoorthy (1984a) found that muscle tissue from yellow perch, bluegill, and black crappie collected from recreational and industrial river zones contained 106, 108, and 103, 100, and 109, 101 ppm zinc dry weight, respectively. Muscle tissue collected from omnivorous and carnivorous fish from industrial and agricultural areas of the lower Great Lakes contained 16 to 88 and 3 to 9 ppm zinc wet weight, respectively (Brown and Chow 1977). Concentrations of zinc in edible tissue collected from fish inhabiting streams contaminated by lead mining in Missouri ranged from 4.0 to 24.0 ppm wet weight (Schmitt and Finger 1987). Whole fish analyzed from the NCBP contained a geometric mean of 21.7 ppm zinc wet weight (Schmitt and Brumbaugh 1990). The maximum concentration was 118.4 ppm wet weight in a carp collected from Lake St. Clair, Michigan.

Residue concentrations of zinc found in fish collected from Yellow and Turkey Creek of SLNWR exceeded the NCBP geometric mean and the 85th percentile concentration of 34.2 ppm wet weight (Schmitt and Brumbaugh 1990). These samples were analyzed at a different time than the Elk and Honeyhouse Creek samples. The high concentrations could be attributed to human error in the collection preparation or analytical processes, or there may be a zinc contamination problem at the refuge.

# Organochlorine Contaminants

# 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane (DDT)

Technical DDT is a mixture of up to 14 analogs and isomers (Moore and Ramamoorthy 1984b). The white, amorphous powder is persistent once in the environment, is transported long distances in the air and water, and is extremely lipophilic. DDT was used as an insecticide for the control of mosquitoes and other insect pests in agriculture. In 1972, EPA restricted the use of DDT for insecticidal use. It was only to be used in case of a public health emergency (Clement Associates 1989b).

DDT does not occur naturally in the environment, so all releases are from its production, use as an insecticide, and runoff from agricultural lands into streams and lakes. Due to the extensive past use of DDT and its persistence, the insecticide and its metabolites are found at low concentrations in most living organisms (Clement and Associates 1989b). DDT bioaccumulates in fish (Moore and Ramamoorthy 1984b, Clement Associates 1989b) and is known to cause eggshell thinning in fish-eating avian species (Haseltine et al. 1975).

The geometric mean residue concentrations in fish collected for the NCBP was 0.26 ppm total DDT (Schmitt et al. 1990). The concentrations found in the fish collected on SLNWR were only slightly above the detection limit and are below the NCBP geometric mean. DDT contamination does not seem to occur on SLNWR.

### Dieldrin

Dieldrin and aldrin (which breaks down into dieldrin) are two insecticides used to control termites, rootworms, and mosquitoes. Dieldrin has been used as a sheep dip and in treatment of wood and mothproofing woolen products (Dynamac Corporation 1989). However, the use of both dieldrin and aldrin has been banned in the United States since 1975.

Like DDT, dieldrin is not found naturally in the environment; therefore, any releases are from insecticidal use and improper disposal. Dieldrin adsorbs tightly to soil and runoff into surface waters is the major source for sediment contamination (from Dynamac Corporation 1989). Dieldrin is toxic to fish. The  $LC_{50}$  for bluegill was reported to be 0.01 ppm dieldrin, and for bass 0.006 ppm dieldrin (from McKee and Wolf 1963).

Dieldrin is persistent in the environment and bioaccumulates through the food chain (Dynamac Corporation 1989). The insecticide is lipophilic, accumulating in fatty tissues of organisms. The concentrations recommended for the protection of predators was 0.1 ppm dieldrin (from Irwin 1988). In a review of the literature, McKee and Wolf (1963) found that feeding experiments with 10 ppm in the diet of pheasants did not affect the adult birds, but there was decreased hatchability of eggs and viability of chicks.

Concentrations of dieldrin in fish collected for the NCBP were at a geometric mean of 0.04 ppm (Schmitt et al. 1990). The significance of this concentration was not discussed. Twelve of the sixteen fish samples from SLNWR exceeded the NCBP geometric mean. Three samples from Honeyhouse Creek, two from Turkey Creek, and one from Yellow Creek exceeded the recommended predator protection level of 0.1 ppm dieldrin. There may be dieldrin contamination in the food base for fish-eating species of wildlife on SLNWR.

#### Chlordane

Chlordane is a complex mixture of isomers, closely related compounds, and by-products, such as those analyzed in this study including cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, heptachlor, and heptachlor epoxide. Chlordane was used in the past for termite control around buildings and for control of insects on crops, especially corn. Chlordane is persistent in soil lasting up to 20 years or more (MDOH 1991). The majority of chlordane in lakes and rivers is from run-off from adjacent agricultural lands or from urban areas where the pesticide was used for termite control.

Organochlorine pesticides, such as chlordane, accumulate in lipid deposits and other fatty tissues of organisms (Moore and Ramamoorthy 1984b). The Missouri Department of Health (1991) has accepted 100 ppb (0.1 ppm) as an action level for human consumption advisories for chlordane in fish. This consumption advisory concentration is for edible portions of species. This whole fish concentration also has been adopted for the protection of predators (NAS/NAE 1972).

All of the total chlordane concentrations in the fish sampled from Honeyhouse, Yellow, and Turkey Creeks are at or above the action level for human and

predator health. There is a chlordane contamination problem at SLNWR according to these data. The chlordane possible could be coming from the surrounding agricultural lands.

# Toxaphene

Toxaphene is a man-made insecticide containing over 670 chemicals (DHHS 1990). Toxaphene was used mainly in the southern U.S. to control insects in cotton and other crops. It also was used to control mites on livestock and to kill unwanted fish in lakes. EPA canceled the registration of toxaphene in 1982 for use as a pesticide, except for use on livestock and in emergency situations (DHHS 1990).

Toxaphene is persistent in the environment, having a terrestrial half-life of up to 10 years in moist, aerobic soils (from FWS 1982). Toxaphene enters surface waters from run-off and deposition from the atmosphere.

The insecticide is accumulated in invertebrates and fish and is toxic to both at low concentrations, 0.0023 to 0.04 ppm and 0.002 to 0.018 ppm, respectively (FWS 1982). Chronic effects at concentrations as low as 0.00039 ppm toxaphene include growth reduction and alterations in backbone composition of collagen, hydroxyprolime, calcium, and phosphorus (Mehrle and Mayer 1975, from FWS 1982). Concentrations of toxaphene in channel catfish tissue were >11 ppm in adults and 3.4 ppm in fry where growth was reduced (from FWS 1982).

Where bone development alterations were reported in adult channel catfish, tissue concentrations were <11 ppm toxaphene (from FWS 1982). In a review of the literature, Eisler and Jacknow (1985:iii) state that "residues in fish tissue in excess of 0.4 to 0.6 ppm wet weight may be hazardous to fish health and should be considered as presumptive evidence of significant environmental contamination".

Concentrations of toxaphene in fish samples collected from SLNWR are less than the hazardous concentration reported above, except for one carp sample from Turkey Creek. This individual sample concentration could be in error, but toxaphene should be analyzed if any other samples are collected during future contaminant studies.

# Recommendations

There are potential contamination problems from dieldrin, chlordane, copper, chromium, manganese, and zinc on SLNWR, according to the data discussed in this report. The major source of these compounds is probably agricultural runoff from the area surrounding the refuge.

If there is concern that populations of fish and wildlife using SLNWR are decreasing or do not seem healthy there should be further investigations into the above compounds. First, an intensive survey of possible sources of the listed compounds should be conducted for the watersheds which drain into the refuge. Then further sampling should be completed to include water, sediment,

and biota of several trophic levels. The biotic organisms also should be necropsied to check for any abnormalities.

The reason whole fish were analyzed for this report is that top fish and wildlife predators consume whole fish. However, data are limited for comparison of the significance of whole fish concentrations to predator populations, and even to the prey species themselves. Therefore, separate tissues or organs should be analyzed as reported in the literature (ie, fatty tissue for organics, liver for metals). This may draw more solid conclusions concerning the possible significance of contamination levels of the listed compounds found in samples from SLNWR.

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